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High-Purity Iron

THE preparation of metals of the highest possible purity has always been a matter of interest to metallurgists. This interest does not arise only on account of theoretical considerations, but is frequently dictated by the practical importance of a high degree of purity in relation to some specific application of the metal. An old-standing example is copper for electrical purposes. More recently the commercial production of aluminium and of zinc in a state of extreme purity has revealed unexpected properties, and there are indications that the magnetic and other properties of iron may be affected by such minute amounts as 0·001 or 0·002 per cent. of impurities such as carbon, oxygen, and sulphur.

The National Physical Laboratory in this country and the National Bureau of Standards in America have recently played a leading part in the production of high-purity iron, and from the latter institution Messrs. J. G. Thompson and H. E. Cleaves* have published another report describing the latest advances that have been made there.

Iron of high purity, in the form of 1 lb. ingots, has been prepared by reducing purified iron oxide to sponge iron, melting the sponge iron, then remelting under hydrogen and solidifying *in vacuo*. The purified iron oxide was made from recrystallised ferric nitrate. It was converted into sponge iron by heating at 500 deg. Cent. in hydrogen until reduction was practically complete, and then raising the temperature to about 1000 deg. Cent. to sinter the surface of the particles. These operations were carried out in silica tubes, and silicon or silica, ranging in amount from 0·008 to 0·024 per cent., was the principal impurity of the sponge iron. For the elimination of silicon the briquetted sponge iron was melted with the addition of 2 per cent. of pure ferric oxide in beryllia crucibles giving ingots of iron containing 0·2 per cent. of oxygen. The oxygen-rich ingots were melted and maintained molten for 45 min. to 60 min. under hydrogen in a high-frequency induction furnace. A period of 30 min. in hydrogen reduced the oxygen content from 0·2 to 0·001 or 0·002 per cent., and these values were not further reduced by longer treatment. After about 45 min., therefore, to allow a margin of safety, the hydrogen inlet to the furnace was closed and the outlet connected to vacuum pumps. During evacuation the temperature of the molten metal was kept approximately constant while the pressure was reduced to 0·02 mm. or less. The power was then cut off and the metal allowed to solidify and to cool to room temperature in the evacuated furnace.

Nineteen ingots, with an average weight of about 1 lb. each, were prepared. They were examined by spectroscopic and chemical methods for the presence of fifty-five possible impurities. The major impurities were non-metallic, chiefly oxygen and sulphur, with traces of carbon, phosphorus, nitrogen, and hydrogen. Copper was the only metallic impurity in seven of the ingots; others contained small amounts of silicon and occasional traces of aluminium or beryllium from the refractories. In most cases the total impurities in each ingot were less than 0·010 per cent.

An account of the properties of this material will be awaited with interest, but so far no tests have been reported except for an interesting observation on the macrostructure of the ingots. It was observed, after preparation of the sections by sawing and grinding, that the surface was covered by parallel striations running lengthwise in the ingot and that these striations persisted through several repolishings and etchings. They were evidence that the surface grinding had work-hardened the metal to an appreciable depth and are of interest as an indication of the considerable strain-hardening which can be undergone by very pure iron.

* Bureau of Standards, *Journal of Research*, July 1939, Vol. 23, p. 163.

Properties of Thin Metal Films

No. II

(*Continued from August issue*)

IN the description already given of the properties of thin metal films (based on Riedel's review of the subject) an important feature was the almost complete non-conductivity of extremely thin films and the failure of relatively thick films to approach the resistivity of the massive metal.

A further advance in the knowledge of the subject comes with the appearance of results obtained by Lovell and by Appleyard and Lovell.[6] In their experiments they pay special attention to the maintenance of stringent conditions of purity, both as regards the film and the surface on which the layer was deposited. By an atomic beam method in a high vacuum they succeeded in depositing layers of the alkali metals on thoroughly cleaned and cooled pyrex surfaces, and the examination of these films resulted in the discovery of entirely new facts. For example, conductivity was observed in films with a mean thickness of 0·1 mμ and even less, and films became quite stable at 4 mμ. At this thickness the specific resistance was only ten times as big, with a normal temperature coefficient, as that of the metal in the massive form, and for thicker layers the limiting value of the resistance was only slightly above the normal value. Immediately after deposition of the layer, a spontaneous increase in resistance was observed. This effect was greater the thinner the

layer, and especially so for very thin layers which had been deposited under conditions of a rising temperature in the base or substrate. It is attributed to the presence of very minute cracks and cavities in the thinnest layers. This is easily understandable in view of the very high surface tension of the metal, under the influence of which any cavity or crack existing in the film will tend to widen. The rate at which it widens depends on the mobility of the atoms of the film. The widening will be resisted by the force with which the metal adheres to the underlying surface. Impurities on the surface modify the adhesion. Except at low temperature and on very clean surfaces the widening proceeds so rapidly that the film breaks up into small islands or aggregates. Under the best conditions, the gaps are filled up before they become too wide. The high resistance of unstable films is to be attributed to cracks. In thick deposits such cracks are bridged over and the conditions for showing very high resistivity do not exist.

The large values of about 200 mμ for the mean free path of the electrons in the alkali metals (as utilised by Lovell and Appleyard for potassium, rubidium, and caesium, in a relationship between the specific resistance and the thickness of the layer) give satisfactory agreement between theory and experiment for alkali metal films, showing that Thomson's theory is adequate in respect of the resistance of films exceeding about 1 mμ in thickness. Moreover, the high resistance of the thinnest layers is put down to the probable formation of cracks resulting possibly from the effect of the temperature at which the layer was deposited, so that all formulæ which do not take this into account must fail in respect of the thinnest layers. Only experiment can decide how far layers of other than the alkali metals will show similar results, but Riedel believes the alkali metals are specially suited for such investigations, and that satisfactory information regarding the mean free path of the electrons is obtainable for other metals, provided the layers can be degassed.

PERUCCA'S HYPOTHESIS

Riedel refers to Perucca's theory, which attempts to explain the steep rise of the specific resistance in the neighbourhood of the "critical" thickness as being due to the presence of a non-conducting layer, a few atoms thick, at the surface of the deposited film. The conductivity should vanish if the deposited film is only double the thickness of this non-conducting layer, and thus the critical thickness is explained. Perucca's theory is quite opposed to other theories. Riedel considers that it cannot explain the anomalies in the electrical conductivity of the thinnest layers because it puts aside structural differences and chemical influences as the cause without bringing forward other plausible reasons. The theory is mentioned at some length by Riedel because it is often quoted, thus giving the impression that it is of the same standing as the other theories, whereas there is no reason to expect that the electrons move between the outermost ions in the lattice less freely than between those within.

SOME OPTICAL PROPERTIES OF FILMS

Optical phenomena associated with thin layers are also discussed, in view of the anticipated association between the optical properties of metals and their electrical conductivity. It is remarkable that the known anomalies of the thinnest layers, found by resistance measurements, are all fully confirmed by numerous investigations on optical behaviour. The agreement also extends to layers which are artificially "aged," indeed, the ageing process can be followed optically. Riedel refers in considerable detail to the optical researches of Murmann and others. Murmann took silver in the form of wedges which had been prepared by depositing the metal from the vaporised state. He then determined their capacity to reflect and transmit visible light, and found that the transmission showed a pronounced increase for layers below about 30 mμ thick and that the reflecting power fell correspondingly. The thicker layers possessed approximately the optical constants of the metal in the massive form. He found similar results using long infra-red waves and the presence of the anomalies in electrical conductivity were confirmed once more. Many interesting observations are referred to. One was the sudden change, depending on the thickness of the film, in the colour of freshly deposited layers of antimony when viewed by transmitted light. Further, the surface was seen to be covered with dark spots, which finally spread over the whole of the surface when the deposition was stopped, and it was believed that here, without doubt, the deposit was changing from the amorphous to the normal crystalline condition. Very interesting observations are recorded for silver and gold, for which reference should be made to Riedel's survey. It appears from such experiments that the optical anomalies of the thin deposits may be suitably explained by the presence of a "colloidal" structure, by which is meant very fine crystallites or minute crystal fragments separated from one another.

STRUCTURE OF FILMS

A most fruitful field of exploration is opened up by the application of X-rays to the determination of crystal structure, and especially, in more recent times, by electron diffraction analysis. The Debye-Scherrer method, as used in X-ray analysis, requires a metal layer at least 40 μ thick, whilst the electron diffraction method is admirably suited for the investigation of very thin films. The latter method has the advantage that only very short exposures are necessary and the calculations are easier; this has resulted in the electron diffraction method being exclusively employed. A considerable amount of work has been done during the last few years. Kirchner has shown for layers about 1 mμ thick that immediately after deposition the method reveals the normal and mostly much broadened interference lines of the lattice of the respective metal. It is concluded that crystallites between 1 and 10 mμ thick are present and further that their orientations lie in all directions. The size of the crystals is found also to increase considerably when the temperature of the layer is just below the melting point of the metal concerned. This is shown by the greater sharpness of the interference lines. If the deposits are not too thin, then certain crystallites take up a specially oriented position. As might be expected, an increase in the temperature of the layer leads to an increased speed of crystal growth. It is noteworthy that the tiniest particles yield lattice constants agreeing to about 1 per cent. with those for the metal when in the massive form as determined by X-rays. These are only just a few of the typical results and investigations by other workers have always tended to confirm them. Thus the lattice structures for thin layers seldom vary from those of the metal in the massive form. When depositing very thin layers of face-centred lattice metals, however, Quarrel made the very interesting observation that an hexagonal close-packed structure always appears first of all and that this becomes transformed into the

normal cubical structure as deposition proceeds. Again, much depends on the condition and structure of the base on which deposition is made. As seems probable, it is concluded that the presence of absorbed gas plays a conspicuous part. Crystal size can be assessed, but it is unfortunate that the accurate determination of the size of the crystals by means of electron diffraction diagrams involves considerable difficulty. For example, the roughness of the surface of the layer affects the diagram when determined by the customary "reflection" method, consequently one is compelled to use the "transmission" method, but then this is limited to very thin layers and even so difficulties are met with.

Although investigations of internal structure all agree in assigning a crystalline form to the film, yet the possibility of the presence at some stage of amorphous constituents in the deposited layers cannot, in Riedel's opinion, be altogether ruled out. What actually happens during deposition has been shown experimentally by Finch and Quarrel.[7] In cathode-sputtering, as well as in depositing thermally from vapours, the metal is actually broken up into atoms, as is demonstrated by passing electron rays through the actual vapour and observing the absence of any interference lines. Hence a crystallite forms immediately the atoms reach the surface on which they are deposited. It is here that an interesting point arises, for the atoms very probably must *move lengthways* along this surface, even at low temperatures, for crystal formation to occur. Appleyard[8] reports that the energy necessary to remove an atom from a very thin layer by vaporisation is only about one-seventh of the heat of sublimation of the metal when in the massive form. In the case of the alkali metals this difference is probably considerably smaller. It may be reasonably concluded that the atoms in a very thinly deposited layer are in a highly unstable state compared with the usual crystalline structure. The agglomeration of the films is therefore possible; whether or not it will take place depends on the mobility of the atoms along the surface of the base on which deposition occurs. The formation of any of these deposits may be visualised then as follows:—The atoms, as a result of their high mobility on the surface of the base on which they are deposited, combine with one another very soon after reaching that surface and form islands. These islands are flattish and at first monatomic in thickness. They expand by growth and form metal crystals as a result of new atoms reaching them and as a result of shrinkage, for the surface tension forces will be very great. Consequently, a film about 1 mμ thick may cover less than one-tenth of the surface of the base. The conduction of electricity will only occur when these gaps in the film are filled up as a result of the islands growing on further deposition. It will occur suddenly and rise very quickly with the increasing number of contacts made between one island and another, and ultimately the conductivity will reach a final end value. The size of the crystals will be very dependent on the mobility of the metal atoms along the base and hence on the temperature of condensation. This mobility varies greatly from one metal to another. For example, the activation energy of cadmium on glass is roughly about six times smaller than for caesium, and in consequence the mobility of the cadmium atoms is very markedly higher than that of caesium atoms. This explains why it is possible in the case of the alkalies to lay down a second layer of atoms before the atoms of the first layer have moved far from their original positions, whereas in the case of cadmium at the same temperature rates of deposition quite impracticably rapid would have to be used to do this.

Riedel recognises that the agglomeration theory as an explanation of the factors affecting the resistance of thin metal films has received ample experimental justification, whereas the theories of Kramer and Perucca receive no such support. There is no reason to think that thin metallic films are ever amorphous, and if they were they would not be expected to show higher resistivity than a molten metal; and there is no theoretical or experimental evidence to suggest that metals show anomalously high resistivity in the neighbourhood of a free surface. Riedel concludes his review by pointing out that, in spite of the value of recent views on the structure of metal films, there still remain some outstanding problems. Of these, it is only necessary to refer to the influence of gas content. In such work as that of Lovell and Appleyard, in which the films were deposited under a high vacuum, this complication does not arise, but a large number of experiments have been made with different metal layers and different gases, and it certainly seems that the bad conductivity of the thick deposits as well as the irreversible reduction in resistance on heating can be very well put down to a high gas content and to the degassing action which occurs on raising the temperature. It is suggested that Kramer's "transformation" is possibly due to the degassing of the films. Riedel gives details of investigations on the effect of gas on the films and refers again in his conclusions to the probably extremely strong influence of the remanent gases on the electrical conductivity as an explanation of the high specific resistance of thick films.

In his article Riedel has certainly succeeded in giving a very complete account of the conductivity and structure of thin metal films, and his bibliography of seventy-three items, all of which receive some notice in the text, should make it a most useful work of reference.

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Protective Coatings for Magnesium Alloys

By T. P. HOAR, M.A., Ph.D.

The development of the ultra-light magnesium-base alloys, with their excellent mechanical properties, has led to considerable research on their protection from corrosion. This is by no means a simple problem, owing to the thermodynamically "reactive" nature of magnesium. The first real advance was the introduction of the "chemical-dip" process employing acid dichromate baths, which produce complex chromic chromate coatings on the metal that are well adapted as foundations for paint; the well-known work of Sutton and le Brocq[1] on these and similar coatings marked a notable step forward in our ability to use magnesium alloys in corrosive surroundings.

Recent French research, reported in three papers in the special number of *Chimie et Industrie* devoted to the "Journées de la Lutte contre la Corrosion," held in Paris in November, 1938, has opened up the way towards perfection in magnesium alloy protection. It is interesting to find that a number of different

procedures have been developed, several of which give great promise.

In the paper by the Société Générale du Magnésium[2] the authors refer first to the possible electrolytic methods of producing non-metallic protective coatings on magnesium, but reject these for the present as being too costly and too irreproducible. They state that progress is being made with a galvanic method of coating without applied current (presumably an "internal electrolysis"), which gives a coating similar to that produced by the chemical-dip method; but they prefer to rely mainly on improved chemical-dip methods followed by painting or lacquering of various types.

The operation of the dipping process is termed by the French "mordançage," a word difficult to translate: "dipping," "pickling," and "mordanting," are all inadequate, for the exact meaning in this connection is "formation by chemical attack of an adherent, protective layer of sparingly soluble products." For accuracy and brevity, the French word is used hereafter in this article.

Four main protective processes are recommended by the Société Générale du Magnésium, for use in different circumstances and for different alloys, as follows:—

(1) Mordançage in the well-known nitric acid/dichromate bath, followed by two coats of air-drying paint. This composite coating stands up to a one-month test in salt spray, without allowing any pitting, and has been found satisfactory for more than a year in atmospheric exposure in aeroplanes and seaplanes.

(2) The same treatment, but using stoving varnishes. Here a stoving at 180 deg. Cent. *before* the first varnish coating is advantageous; doubtless some sintering of the chromate coating takes place, and the further stovings at 180 deg. Cent. do not then disturb it. The second varnish coating is pigmented with aluminium. This process is recommended for conditions where severe temperature changes are likely to occur, and satisfactory tests have been made with temperatures down to −50 deg. Cent.

(3) For alloys containing more than 7·5 per cent. aluminium, or when alteration in dimensions has to be reduced to a minimum, a milder bath, practically identical with bath 2A of Sutton and le Brocq, is recommended for mordançage, viz.:—

Ammonium sulphate, kilos.	3
Ammonium dichromate, kilos.	1·5
Potassium dichromate, kilos.	1·5
Ammonia solution, S.G. 0·92, kilo.	0·5
Water, litres	100

The sheets, carefully degreased, first in trichlorethylene and then in boiling 2 per cent. caustic soda for thirty minutes, are placed in the boiling dichromate bath for thirty minutes, and are then dried. The grey or black coating is treated as before with stoving varnishes.

(4) For alloys containing 10 per cent. aluminium the following bath (bath 4 of Sutton and le Brocq) is recommended for mordançage:—

Powdered alumina, kilo.	1
Chromic anhydride, kilos.	10
Hydrated magnesium sulphate, kilos.	5
Caustic soda, kilo.	1
Water, litres	100

The bath is used at 95 deg. Cent. and the work immersed for thirty seconds only, when a bronze-coloured film is produced. Either air-drying or stoving varnishes are then applied as in the other procedures, and very good protection is obtained.

It is emphasised in the paper that careful degreasing before mordançage, and before painting if the work has become greasy, is essential for the best results.

The paper by J. Frasch[3] describes several new electrolytically formed coatings. Frasch points out that mordançage gives an inherently porous coating, and further that the complex chromate material is neither insulating nor especially inert chemically, properties that he considers very desirable in protective coatings. He has therefore been led to develop electrolytic procedures that give very promising results. The methods may be divided into two groups, those using acid and alkaline baths respectively.

(1) *Alkaline Baths.*—Baths containing caustic alkali with or without alkaline salts such as carbonates or phosphates give, when operated below about 10 volts in the cold, coatings of magnesium oxide at the magnesium anodes. Unlike the well-known anodically produced oxide coatings on aluminium, these coatings are not protective, being porous and often non-adherent; the specific volume of magnesium oxide is too small for a continuous coating to be formed. Some improvement is effected by the addition of silicate to the caustic alkali bath, and by the use of higher voltages; furthermore, these films can be rendered insulating and fairly protective by a subsequent treatment in a hot alkaline silicate solution, which has a "vitrifying" action and makes the film less porous. But an altogether superior silicate coating can be produced by A.C. electrolysis, with a voltage above 50 volts, in a bath with a comparatively high $SiO_2 : Na_2O$ ratio. The coating is transparent, very adherent, and forms a good basis for paint. Also, although slightly porous, it is itself quite protective against saline liquors, apparently because the pores close up owing to slight hydrolysis of the coating with increase of its specific volume; thus specimens have withstood fifteen days in sea water without any attack on the underlying metal. The "vitrifying" process already mentioned further improves the coating, enabling it to withstand a month in sea water without attack; these vitrified coatings, however, are not good undercoats for paints, doubtless because their lowered porosity does not facilitate absorption and "keying" of paints.

(2) *Acid Baths.*—The principle here is different. Instead of the anodic production from the metal of insoluble magnesium compounds, the deposition of a coating of chromium or manganese oxides is achieved by A.C. electrolysis in chromic or permanganic acid baths. In the case of the chromic acid bath, the coating formed has a composition between CrO_2 and Cr_5O_9, and is evidently produced by cathodic reduction of the chromic acid. Suitable A.C. voltages are 5 volts for a 12 per cent. chromic acid solution and 7 volts for a 5 per cent. solution. Electrolysis is continued until the current, which rises some 5–15 per cent. of its initial value, remains constant; further electrolysis is then disadvantageous. The coating obtained is black or violet-black in colour, and is adherent and non-reactive. The bath can be improved by the addition of small amounts of chromic sulphate or manganous carbonate, which give it an initial "pickling" action that results in a more even coating. The permanganic acid bath, made by adding considerable amounts of manganous carbonate to chromic acid solution, when carbon dioxide is evolved and chromium oxides are precipitated, is operated with A.C. at 8–25 volts; the current falls during electrolysis to 40 per cent. of its initial value, and a brown coating of manganese

oxides is formed. Both these coatings are very protective, and are also good supports for paints; the chromium oxide coating is further improved by immersion in hot alkaline silicate solution (when chromium silicates are formed), but the manganese oxide coating is harmed by this treatment. We may note that, in principle, the production of these coatings is similar to that of dichromate mordançage; but the reduction of the chromium (or manganese) acids to insoluble complex oxides of lower valency is effected largely by the cathodic phase of the A.C., rather than by the magnesium itself, so that the coatings may be expected to be thicker and less porous.

Frasch concludes with a comparison of the corrosion, as indicated by the mechanical properties, of specimens treated in some of the baths he describes. It may be noted from his results (Table I) that the

TABLE I.—*Corrosion Tests by J. Frasch; Alloy T 2; Sheet Specimens*

Treatment.	Corrosion.	Tensile strength.	Elongation.
		Kg./mm.².	Per cent.
None	None	21·6	10
None	None	20·6	8
Chromic acid bath	30 days in sea water	24·6	8
Ditto	30 days salt spray ...	24·9	9
Silicate bath	30 days in sea water	21·0	6·9
Ditto	30 days salt spray ...	20·0	5·25
Dichromate mordançage	15 days in sea water	9·5	0·3
Ditto	30 days salt spray ...	14·3	0

chromic acid and silicate electrolytic treatments, especially the former, compare very favourably with the ordinary dichromate mordançage, with respect to their protective value when unreinforced by paint coats. A comparison of painted specimens would also have been of value, since mordançage is used only in conjunction with paint.

The paper by J. Pomey, E. Fourquin, and X. Hardy,[4] of the Usines Renault Laboratory, is perhaps even more interesting than those already reviewed, for the authors have approached the problem in an exceptionally logical way. Their coatings are all based on the well-known sparingly soluble nature of magnesium fluoride, but a whole range of mixed basic fluorides has also to be considered.

In their researches the authors first found that clean magnesium, when anodised in 10 per cent. potassium fluoride solution at 50 deg. Cent., with an initial current density of 0·1 amp./dm.², builds up a very thin insulating film of magnesium fluoride in two minutes, the current falling to 10 per cent. of its initial value and the bath voltage rising to the 40 volts of the supply used. This film, however, disappears when washed for fourteen hours with water, alkaline solutions, or chloride solutions, as shown by re-anodising the specimen, when the film builds up again with similar electrical characteristics; but washing in 3 per cent. potassium fluoride solution scarcely affects the film, for on re-anodising, the insulating condition is attained within a few seconds. Since the fluoride film is evidently appreciably soluble except in solutions containing an excess of a soluble fluoride, the authors turned to more alkaline fluoride baths (containing carbonate, borate, &c.), and obtained mixed basic fluoride coatings. When these are washed with water and the specimens re-anodised in 10 per cent. potassium fluoride solution, the insulating condition is more quickly regained than in the previous case, showing that the films are less soluble than the normal fluoride, as expected. Moreover, the films are thicker than the pure fluoride, owing to the presence of ions other than fluoride ion in the bath. The next step was to augment the thickness still further by the use of A.C.; the cathodic part of the cycle does not reduce the basic fluorides formed by the anodic part, but seems to render the film more porous and thus to promote its thickening. If now the D.C. process is applied to the film thus formed, it is rendered insulating; the two processes are largely additive. Finally, the authors desired to make a coating that would have good mechanical as well as corrosion resistance. This is achieved by a preliminary treatment in cold potassium permanganate solution acidified with acetic acid, which gives a porous, but flexible, coating of oxides of manganese. The A.C. and D.C. electrolytic processes are then applied to the material, and a very good mechanically and corrosion-resistant coating is obtained.

The threefold process, in its final form, may be summarised:—

(1) One hour in cold 5 per cent. potassium permanganate, 5 per cent. acetic acid solution.

(2) Thirty minutes at 50 deg. Cent., A.C. at 40 volts (effective), in 5 per cent. sodium fluoride, 2 per cent. sodium carbonate* solution.

(3) Thirty minutes at 50 deg. Cent., D.C. at 40 volts, in 5 per cent. sodium fluoride† solution.

Comparative corrosion tests in "artificial sea water" were made, for a 1·8 per cent. manganese alloy; some of the results are given in Table II. The threefold treatment compares very favourably with dichromate mordançage, being as good as Frasch's chromic acid treatment. It is again unfortunate that no painted specimens are reported.

The authors have also worked out a somewhat simpler, but more lengthy, treatment as follows:—

(1) One hour at 50 deg. Cent., A.C. at 40 volts (effective), in 4 per cent. sodium fluoride, 4 per cent. sodium borate solution.

(2) Four hours at 80 deg. Cent., in 1 per cent. potassium hydroxide, 10 per cent. potassum fluoride solution.

This is said to give results equal to those obtained by the threefold treatment for the 1·8 per cent. manganese alloy. For the 6 per cent. aluminium alloy the former process is replaced by:

(1*a*) Forty-five minutes at 50 deg. Cent., A.C. at 60 volts (effective), in 3 per cent. ammonium fluoride, 10 per cent. ammonium oxalate solution, the second process being the same, but carried on for five hours. This twofold process gives protection that is initially excellent, but not so lasting as that conferred on the 1·8 per cent. manganese alloy by the threefold treatment.

It is interesting to note that the most favourable treatments arrived at by these three different researches have two general principles in common: (1) the formation of a durable, but porous, coating of insoluble chromium or manganese oxides; (2) the filling up of the pores. The Société Générale du Magnésium prefers paint or varnish, Frasch prefers silicates, and Pomey and his colleagues use mixed basic fluorides for this latter purpose. Several of the electrolytic processes seem to have great advantage over simple dichromate mordançage where no subsequent paint or lacquer coating is to be applied; it is also quite probable, but it has not yet been demonstrated, that some of the electrolytic treatments provide the better undercoats for paints. We must also remember that painting is often distinctly disadvantageous from a weight point of view, and that chemical coatings that do not need further reinforce-

* Or 5 per cent. NaF, 4–5 per cent. $Na_2B_2O_7$.

† Or 3 per cent. NaF, 3 per cent. NH_4F.

ment are very desirable for many purposes. These promising French treatments are probably not the last word, for clearly many more variations on the silicate, fluoride, and oxide themes are possible. It appears to the reviewer that further work might well be directed towards the simplification and shortening of the electrolytic treatments, with a view to facilitating their practical applications and to lowering

TABLE II.—*Corrosion Tests of J. Pomey et al.; Alloy 1·8 per Cent. Mn; Sheet Specimens in "Artificial Sea Water," 3 per Cent. NaCl, 0·3 per Cent. $MgCl_2$ Solution*

Treatment.	Time of corrosion.	Hydrogen evolved.	Tensile strength.	Elongation.
	Days.	Ml./dm.².	Kg./mm.².	Per cent.
None	0	0	23·6	11·2
None	2	430	—	—
Mordançage	,,	110	19·6	5·8
Treatment :				
(1)	,,	86	17·2	3·7
(2)	,,	24	23·2	9·3
(3)	,,	13	23·0	12·3
(1)+(2)	,,	17	22·6	12·7
(1)+(3)	,,	13·7	21·6	13·8
(2)+(3)	,,	14·3	22·5	10·75
(1)+(2)+(3) ...	,,	6·75	23·4	11·5
(1)+(2*a*)+(3*a*) ...	30	134·5	22·5	10·2

Mordançage : 1 min. in the cold in 18 per cent. $K_2Cr_2O_7$, 18 per cent. HNO_3.

Treatment :

(1) ... 1 h. in the cold in 5 per cent. $KMnO_4$, 5 per cent. CH_3CO_2H.

(2) ... 30 min. at 50 deg. Cent., A.C. at 40 volts, in 5 per cent. NaF, 2 per cent. Na_2CO_3.

(2*a*) ... Ditto, in 5 per cent. NaF, 5 per cent. $Na_2B_2O_7$.

(3) ... 30 min. at 50 deg. Cent., D.C. at 40 volts, in 5 per cent. NaF.

(3*a*) ... Ditto, in 3 per cent. NaF, 3 per cent. NH_4F.

their costs; this would meet the present objections of the protagonists of simple mordançage. We may doubtless look forward to such further improvements, while congratulating the authors on the very considerable progress already made.

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Sigma Phase in Iron-Manganese-Chromium Alloys

IN the course of numerous investigations of the mechanical properties of the high-chromium-manganese steels,[1] the influence of constitution has been recognised and in particular the necessity of keeping the composition within such limits as to avoid the possibility of the precipitation of the brittle σ-phase on tempering. For example, M. Schmidt and H. Legat gave a limit of composition for the appearance of the σ-phase on reheating at 700 deg. Cent. without actually defining the phase boundaries more definitely. It appears unlikely that the plain chromium-manganese steels will prove to be effective substitutes for chromium-nickel steels. Legat[2] in his latest investigations of an 18 : 9 chromium-manganese steel concluded that the most satisfactory properties in steels of this type were exhibited by a steel containing chromium 18 to 19, manganese 5·6 to 6·0, nickel 3·5 to 3·8, and molybdenum 1·6 to 1·8 per cent. Nevertheless, the constitution of the iron-manganese-chromium ternary system is a matter of practical importance as a basis for the interpretation of the structure of the more complex alloys, and also has a theoretical interest in its resemblance to corresponding regions of the iron-nickel-chromium alloys. Such a resemblance might be expected, since manganese, like nickel, promotes the formation and stability of austenite in iron-chromium alloys, but is less effective for an equal concentration, the austenite-retaining effect of manganese being about half that of nickel. An alloy with 15 per cent. of chromium and 8 per cent. of manganese consists of equal amounts of ferrite and austenite, but increasing the manganese to 50 per cent. will not render a low-carbon alloy of this chromium content completely austenitic. Moreover, the σ-phase in chromium-manganese steels bears a close similarity to the corresponding phase in chromium-nickel steels. Until recently the most complete investigation of the iron-chromium-manganese system was that of C. O. Burgess and W. D. Forgeng,[3] of whose diagram a section is shown in Fig. 1. This has since been supplemented by work on

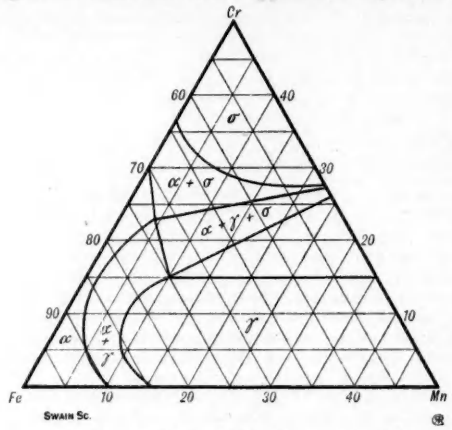

FIG. 1—*Isothermal Section Through the Iron-Chromium-Manganese System at 650 deg. Cent. (Burgess and Forgeng)*

the system recently reported by P. Schafmeister and R. Ergang.[4] The main object of this work was to ascertain, as definitely as possible, the region of stability of the σ-phase in alloys tempered for fifty hours or more at 650 and 750 deg. Cent. For this purpose the alloys prepared by Brühl[5] were studied micrographically and by X-ray, magnetic and hardness tests. These alloys were water quenched after half an hour at 1200 deg. Cent., reheated for eight hours at 700–800 deg. Cent. and again quenched in water. Additional alloys, covering the higher ranges of chromium and manganese content, were made in a high-frequency furnace. They were water quenched after half an hour at 1200 deg. Cent., reheated for eight (or sometimes fifty hours or more) at 650–750 deg. Cent. and cooled in air.

From the data obtained the isothermal section at 700 deg. Cent. was constructed up to 90 per cent. of chromium and 50 per cent. of manganese. The diagram was not completed for the higher chromium and manganese contents, as changes occurring in the chromium-manganese binary diagram and their effect on the ternary system were not completely worked out. In the section (Fig. 2) four single-phase fields appear (two α, one γ, one σ), five two-phase fields (two α+σ, two α+γ, one γ+σ), and two three-phase fields (α+γ+σ). The structure of a few typical alloys and the accompanying changes of Brinell

hardness are indicated in the Table for alloys containing less than 0·1 per cent. of carbon. In the 30 per cent. chromium series, which consist of the α solid solution when quenched from 1200 deg. Cent., the decomposition of the α is very sluggish in the low-manganese alloys, which are only partially transformed to σ. For example, the 30 : 5 chromium-manganese alloy was little affected by eight hours' heating at 700 deg. Cent. and required 500 hours at that temperature to cause a fall in magnetic saturation value from 11,700 to 5500 gauss and a rise in Brinell hardness from 190 to 425. In the 30 : 10 chromium-manganese alloy the magnetic saturation value fell and Brinell hardness rose much more rapidly, attaining 670 after eight hours at 700 deg. Cent. With higher manganese the alloys transform completely into the σ-phase. The boundaries of the high-chromium alloys are uncertain, as they were all found to have taken up nitrogen during melting. The amount of nitrogen absorbed increased with chromium content from about 0·14 per cent. with 45 per cent. of chromium to 0·58 per cent. with 60 per cent. of chromium. They were all very brittle. The line U U¹ represents the boundary between the alloys which on quenching from 1200 deg. Cent. were non-magnetic (right of U U¹) and those which were magnetic (left of U U¹). With higher carbon content the γ-region in the 700 deg. isothermal section was enlarged and the σ-region restricted. Thus, the alloys with 20 per cent. of chromium and 1 per cent. of carbon, after annealing, are all fully austenitic and free from σ-precipitation. With this carbon content it is not until 30 per cent. of chromium is reached that the alloys are ferritic when quenched, and precipitate σ on reheating. The transformation to the σ-phase was complete in the alloy containing chromium 30, manganese 15, and carbon 1 per cent. The reversion of the σ to the α phase on heating occurs at 800–1000 deg. Cent., the transformation temperature being higher the further the alloy lies within the σ-region.

The form of the iron-chromium-manganese diagram bears some resemblance to that of the iron chromium-nickel alloys.[6] They differ chiefly in the extent of the region of stability of the σ-phase. This region tends to narrow down on passing from the binary iron-chromium to the ternary alloys. The σ-phase dissolves only about 10 per cent. of nickel and no longer appears, associated with γ, above chromium 35, nickel 33 per cent. In iron-chromium-manganese alloy the width of the σ-region increases on passing into the ternary system. The σ-phase can dissolve up to 35 per cent. of manganese and still exists, associated with γ, in the alloy of the highest manganese content examined, viz., chromium 20, manganese 64 per cent. Not only is the σ-phase found over a much wider region of concentration in the manganese than in the nickel alloys, but it is much more readily precipitated by a reheating of short duration, both of which facts serve to restrict the useful range of composition of the plain iron-chromium-manganese alloys.

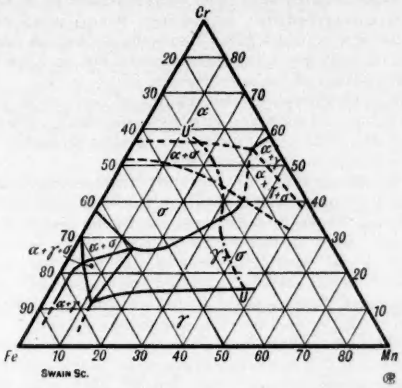

FIG. 2—*Isothermal Section Through the Iron-Chromium-Manganese System at 700 deg. Cent. (Schafmeister and Ergang)*

TABLE.—*Structure and Hardness of Iron-Chromium-Manganese Alloys after Different Treatments*

Composition.		W.Q. 1200 C.		W.Q. 1200 C. 8 hr. 700 C. w.q.		W.Q. 1200 C. 8 hr. 800 C. w.q.	
Cr.	Mn.	Structure.	H.	Structure.	H.	Structure.	H.
15	5	α+martensite	280	α+martensite	255	α+martensite	270
15	10	α+γ	210	α+martensite	310	α+martensite	315
15	15	α+γ	185	γ+σ	225	γ+σ	222
20	5	α+martensite	190	α+martensite	155	—	155
20	10	α+γ	200	α+γ+σ	300	—	220
20	15	α+γ	190	γ+σ	390	—	370
27·5	16	α	260	σ	765	—	—
30	5	α	190	α+σ*	425	—	—
30	10	α	220	(α)+σ	670	—	685
30	15	α	300	σ	650	σ	685

* After 500 hours at 700 deg. Cent.

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[2] *Metallwirtschaft*, 1938, 17, 509.
[3] *Metals Technology*, 1938, 5, No. 3.
[4] *Archiv für das Eisenhüttenwesen*, April, 1939, 1938–39, 12, 507.
[5] *Archiv für das Eisenhüttenwesen*, 1936–37, 10, 243.
[6] *Archiv für das Eisenhüttenwesen*, 1938–39, 12, 459; see THE METALLURGIST, June, 1939, page 38.

Yield Point Phenomena

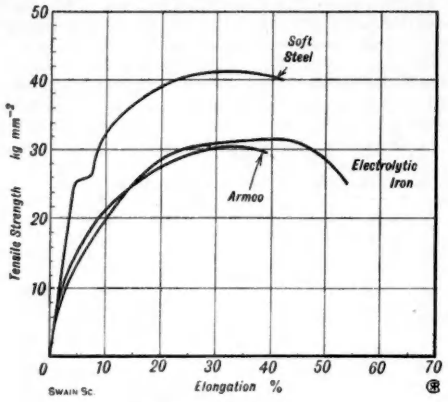
THE appearance of Lüders' lines and of the *palier*,* or yield point extension in the stress-strain curve, which occur at "yield" in soft steel, are familiar phenomena associated with the tensile test. In an illustrated description of experiments on low-

* The term *palier* (signifying the landing of a staircase) used by Kuroda is not a very suitable term for the yield point extension, as the true curve shows a fall of stress at the yield point, rather than a horizontal portion.

carbon steels and on non-ferrous alloys, M. Kuroda[1] postulates a theory of a "honeycomb" structure of envelopes of carbide and impurities surrounding ferrite crystals, in an attempt to explain the phenomena and their dependence on the effect of cold work, &c. Reference has recently been made to this theory in relation to other explanations put forward for the phenomena of yielding and ageing.[2]

The essential feature of the apparatus used is the measurement of load by the elastic deflection of a steel beam, the load being applied at the centre of the span. The deflection is measured through an optical lever system and is recorded photographically on bromide paper carried on a drum, the rotation of which is synchronous with the straining mechanism.

Arrangements were first made to photograph the surface of the specimen under test. Specimens were strained at the rate of 1 cm. per hour, photographs being taken at intervals of half or one minute, corresponding points being marked on the load extension diagram by breaking the light beam to the recording drum whenever exposure was made. The tests



Load-extension Diagrams

revealed that the appearance of Lüders' lines coincided entirely with the fall in load at yield and that they continued to form along the specimen until the *palier* was complete; that is, when the load had again reached the value at yield point. Further tests, made with an extensometer, showed that Lüders' lines appeared when the limit of proportionality was reached. Unfortunately, axial loading shackles were not used, so that in his tests the author frequently found that bending prevented proportionality being continued up to the "upper yield point," as found by Docherty.[3]

Attempts at observations of structural changes were made during testing. Photo-macro and micrographs were taken of the Lüders' lines and although slip was observed by adopting the Schlieren method of illumination, no conclusive evidence was found to justify stating that changes in structure had occurred at yield. At stresses beyond the yield point it was found that crack lines appeared in the microstructure causing block movement of grains analogous to rock deformation. Such blocks moved as units, independently of crystalline direction or grain boundary. As the carbon (pearlitic) content of the steel increased such crack lines passed through the ferrite and avoided the pearlite grains.

The effect of various heat treatments by quenching and tempering was such that the quenched samples had no *palier* at yield, but this was recovered by subsequent tempering, the recovery becoming more marked as the tempering temperature increased. Cold-rolled steel did not recover the yield phenomena until the structure had been recrystallised by annealing, low-temperature annealing being ineffective. Cold work in tension, after ageing by boiling in water, revealed that recovery takes place so long as the structure has not become fibrous.

The diagrams show the results of tests with pure irons compared with the stress-strain relation for soft steel. No yield phenomena are present in either the Armco or the electrolytic irons.

It was thought that if the yield phenomena appeared in non-ferrous metals and alloys the same mechanism producing these in soft steel might be assumed to produce them in the former. Exhaustive tests on 70 : 30 brass and phosphor-bronze (96 per cent. copper), both metals reported as revealing yield phenomena, failed to reproduce them, as also did tests on pure copper and 95 : 5 aluminium-bronze.

Yield point phenomena are thus characteristic of soft steel in the annealed state where the structure is mainly ferrite grains honeycombed with a layer of boundary cementite. The explanation must therefore lie with this structure, since if ferrite be the cause then pure iron would show yield phenomena; or if cementite or pearlite are the reason then they will appear strongly in white pig iron or hard steels. Previous theories have, in the author's opinion, neglected to explain the phenomena on the basis of the structure of soft steel which alone reveals these conditions.

Soft steel can be visualised as composed of ductile ferrite grains filling the cells of a honeycomb, the walls of which are the hard boundary cementite. If, then, this structure is destroyed the yield point phenomena must vanish and appear again only when the structure is recovered. Such destruction is accomplished by quenching, when the boundary cementite is fragmented by the rapid cooling into the unstable condition between austenite and fully segregated boundary cementite. The tests revealed that the yield phenomena vanished in the quenched steel, but reappeared by tempering and annealing, the latter causing the fragments to form again a continuous film about the ferrite grains. This argument also holds for non-existence of the yield point extension after mechanical cold work by rolling or drawing.

The mechanism of failure under conditions of stress in a heterogeneous structure is allied to the stiffness of the constituents. In the honeycomb structure of ferrite and boundary cementite, the brittle cementite, receiving the same strain as the ferrite, will fail first. An instantaneous addition of load, originally carried by the hard cementite, then falls on the soft ferrite which deforms plastically an amount proportionate to the applied load. This gives the *palier* or yield elongation, the breakdown of the boundary structure appearing as the Lüders' line. At ordinary temperature (15 deg. Cent.) the breakdown occurs in narrow bands (Lüders' lines), which begin at one point in the parallel part and spread outwards to cover the whole. The transfer of load to, and consequent extension of, the ferrite are in tiny increments, so that the load extension diagram at yield shows constant load during the *palier*. As the testing temperature increases, however, as tests showed, discontinuities in the load extension curve at yield appear as zigzags. This is explained if we assume that the boundary structure toughens with increased temperature owing to carbon absorption in the ferrite. The failure of the tough,

but weakened, boundary, therefore, is more violent on account of the release of a larger quantity of stored energy so that discontinuities become evident.

As already pointed out, the pure irons or higher-carbon steels fail to show marked yield phenomena. On the basis of this theory, when the boundary structure is weakened by lack of carbon—as in pure irons—quenching, or grain growth, the characteristic *palier* or Lüders' lines fails to appear. Similarly, increase in carbon content merely increases the pearlite which inhibits the deformation at yield.

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The Influence of Alloying Elements on the Scaling and Decarburisation of Steel

PRECISE information on the influence of alloying elements on the scaling properties of steels is meagre, in spite of the numerous researches that have been carried out on this subject. This is chiefly due to the fact that a number of variables, such as temperature, oxidising medium and composition of steel, which so effectively influence the scaling properties, are not comparable in different investigations; and until all these factors have been examined it will be impossible to correlate the results obtained by different workers and thus build up a comprehensive knowledge of the subject. Another factor which discourages work on this problem is the difficulty of obtaining a series of steels with a single alloying element in the correct proportions, while the other elements in the steels are kept at a constant value.

Much of the scattered information on the effect of alloying elements on the scaling properties and decarburisation of alloy steels has been collected together in a recent article by Hans Schrader.[1]

Before discussing the information contained in Schrader's paper it may be advisable to point out that a comparison of the scaling properties of any two steels should always be made with reference to the same temperature and oxidising atmosphere, and it must not be assumed that the relative value of the two steels will be the same in a different atmosphere or even at a different temperature. For example, it has been shown[2] that in a neutral furnace atmosphere at 1000 deg. Cent., a 4 per cent. Si steel or a 12 per cent. Cr steel has a higher resistance to oxidation than a plain carbon steel, but if sulphur is present in the furnace atmosphere the plain carbon steel scales more slowly than either the 4 per cent. Si or the 12 per cent. Cr. Also, changing the scaling temperature from 1000 deg. to 1150 deg. Cent. in the neutral atmosphere containing 0·2 per cent. SO_2 increases the scaling rate of a plain carbon steel 2½ times, while the increase with a 4 per cent. Si steel is four times.

Unfortunately, in his article Schrader has not in all cases made it quite clear what the scaling atmosphere was, and when furnace atmospheres are mentioned the presence or absence of free oxygen or sulphur dioxide is not indicated.

In the first part of his review, Schrader concludes from results which he obtained by heating a number of steels containing a single alloying element in an ingot reheating furnace at 1200 deg. Cent. that the influence of alloying elements, when present from 3 to 6 per cent. was roughly similar. There were, however, differences in the degree of penetration of oxide scale into the steel. A series of photo-micrographs which illustrate the penetration of the oxide into the metal is given, the least penetration being shown by a 3 per cent. Cu, 3 per cent. Al, 3 per cent. W, and a 3 per cent. Cr steel, and intense penetration, by a 3 per cent. Mo, 6 per cent. Co, and a 6 per cent. Ni steel.

Experiments carried out at Leeds University and recently published[2] do not confirm Schrader's conclusions, it having been found, for example, that a 5 per cent. Ni, 4 per cent. Si, and an 8 per cent. Al steel give widely different rates of scale formation. Further, the degree of penetration of oxide into the metal is greatly influenced by the presence of sulphur dioxide or free oxygen in the furnace atmosphere, but not to the same extent for different steels.

In considering the effect of single alloying elements on the rate of oxidation of steel, Schrader quotes the work of a number of investigators [3 4 5 6] as indicating that aluminium diminishes the rate of oxidation, while the work of Scheil and Kewit[7] and also Piwowarsky[17] show that the first additions of aluminium up to 2 per cent. actually increase the rate of oxidation. This increase in the oxidation rate of aluminium has not been confirmed by recent experiments, where it has been found that at 1000 deg. Cent. in furnace atmospheres free from sulphur dioxide 1 per cent. Al is as effective in decreasing the rate of oxidation of a steel as 4 per cent. Si.

With regard to beryllium two investigations are quoted, one by Scheil and Kewit[7], which demonstrates that beryllium up to 4 per cent. did not show any protective influence; the other, by Laissus[28], in which an improvement was found in oxidation resistance when ingot iron was given a surface coating of ferro-beryllium by cementation.

The only reference to boron is the work of Fry,[8] who suggests that with highly alloyed steels such as 30 per cent. Cr steel, any boron in the steel forms boron oxide which acts as a flux and destroys the protective film of chromic oxide.

Chromium is regarded as an element which confers on steel resistance to oxidation by all the investigators quoted, with the exception of Schiel and Kewit, who maintain that with less than 2 per cent Cr there is an increase in the rate of oxidation.

It has been stated by some investigators that the resistance to oxidation does not increase proportionately with the chromium additions, but in an irregular or step-wise manner. The only evidence which Schrader adduces for this conclusion is a curve published by Schottky and Houdremont[10] in "The Corrosion of Metals," though the results plotted in this figure do not justify the curve shown.

Schrader does not refer to McQuigg,[26] who concluded that there is a marked increase in resistance to oxidation with chromium additions up to 9 per cent., from 9 to 20 per cent. the resistance to oxidation continues to increase, but at a slower rate, while above 20 per cent. Cr there is another sharp increase in the resistance to oxidation.

The influence of copper has not been examined extensively and the only reference to it is the work by Bennek,[11] in which the presence of up to 0·25 per cent. Cr is shown to have a slight effect in diminishing the rate of oxidation in air. Bennek also shows in this work that the first additions of nickel have a retarding action on the oxidation of steel in

air, this effect increasing with higher percentages.

Schrader states that no information is available on the influence of manganese except for the results published by Burns, in which a 1 per cent. Mn spring steel showed a higher rate of oxidation than one containing 0·6 per cent. Mn. Since the publication of Schrader's paper it has been shown that manganese,[2] even up to 13 per cent., has no appreciable effect on either the mechanism or rate of scale formation of plain carbon steels in furnace atmospheres.

Though molybdenum is usually regarded as an element which accentuates scaling tendencies, Scheil and Kewit[7] are reported to have found that molybdenum has a beneficial effect in increasing the resistance of a steel against oxidation and this has been confirmed by Scherer,[14] Brief,[15] Houdremont and Schrader,[16] with high-speed steels to which molybdenum has been added.

Phosphorus has only a slight effect on the rate of oxidation, but influences the type of scale formed, making it adherent.

Silicon effectively increases the resistance of a steel to oxidation, but Portevin and his collaborators[6] state that it is not as effective as similar quantities of aluminium or chromium. Scheil and Kewit, however, have published results which show that at 1000 deg. Cent. the first 2 per cent. Si, and at 1200 deg. Cent. the first 4 per cent. Si added to a steel causes an increase in the rate of oxidation. Other workers have shown entirely different results to those put forward by Scheil and Kewit.

Very little work has been done on the effect of vanadium on oxidation phenomena. Tammann and Siebel,[27] from an examination of temper colours, concluded that vanadium had a beneficial influence, though Laissus[28] could find no appreciable effect even with an addition of 4 per cent. Va to a steel.

Schrader from his own experiments has concluded that additions of tungsten increase the resistance of a steel to oxidation, but Fry[9] reports that when added to a 20 per cent. Ni, 25 per cent. Cr heat-resisting steel it had a deleterious effect.

With plain carbon steels it has been shown that in furnace atmospheres free from sulphur dioxide the rate of scale formation at 1000 deg. Cent. decreases uniformly with increasing carbon content. This is not in agreement with Murphy's[29] results, which show a maximum in the rate of oxidation at 0·3 per cent. C. No other investigators have reported this maximum at 0·3 per cent. C, and indeed it is difficult to imagine why it should exist.

Schrader concludes from the results obtained by Piwowarsky[17] and Dickinson[18] and also Murphy,[12] who used air and the products of combustion of coal gas respectively as oxidising media, that while highly alloyed steels show important differences in scaling rate, steels containing such small amounts of the alloying elements as 1 or 2 per cent., do not show any marked differences in the rate of scale formation at the lower heat treating temperatures, *i.e.*, up to 700 deg. Cent.

Heat resistance in alloy steels is explained by the formation of protective oxide layers through the preferential oxidation of the alloying elements whose oxides have higher heats of formation than iron oxide. Of the elements which can be included in this class, the most effective are Al, Cr, and Si, and of less importance W, Va, Ti, Zr. This explanation is not complete, since it is necessary for the oxide of the alloying element to form a continuous film at the scale metal interface and to possess a low solubility for iron.

Alloying elements whose heats of oxidation are less than that of iron—for example, Cu and Ni—accumulate at the scale or metal interface and generally have only a minor influence on the scaling rate. Elements such as boron, which form low melting point oxides, would naturally have a deleterious effect on a protective oxide coating, while elements which form volatile oxides, such as molybdenum, might disturb and render porous the protective oxide layer.

At this point it may be of value to indicate again the important influence which the presence of sulphur dioxide in the atmosphere can have on the scaling properties of alloy steels. Steels containing 12 per cent. Cr or 8 per cent. Al which possess a high degree of resistance in sulphur-free furnace atmospheres scale more rapidly than a plain carbon steel when sulphur dioxide is admitted to the atmosphere.

In the second part of his paper Schrader considers the effect of alloying elements on the susceptibility of steels to become decarburised in certain atmospheres. The investigations of Baukloh with Guthman[19] and Kronenfels[20] are quoted as being the most important on this subject. In the earlier research, industrial steels were used, but owing to the occurrence of certain anomalies the later research was carried out on specially prepared steels containing the single alloying element. In these researches it was found that aluminium decreased the rate of decarburisation, but at temperatures near 700 deg. Cent. the opposite was true for high-carbon steels.

Schrader in his experiments with Houdremont[23] found that aluminium decreased the decarburisation tendencies of a steel except when present in amounts below 0·3 per cent. This effect with low additions of aluminium is, according to Schrader, due to a refinement in crystal size, producing a large number of crystal boundaries which interfere with the decarburisation process. He does not explain, however, why the crystal boundary should act in this manner.

There is general agreement that chromium increases the resistance of a steel to decarburisation. The formation of stable carbides of chromium explains why chromium should have this effect. Campbell, Ross and Fink[21] found that a steel contining 14 per cent. Cr showed no decarburisation after several days' treatment at 950–1000 deg. Cent. in an atmosphere of moist hydrogen. The slight increase in rate of decarburisation reported by Baukloh and Kronenfels with chromium contents below 0·3 per cent. may be due to some effect which this small addition of chromium has on the structure of the steel.

Neumann[22] has shown that the beneficial effect of chromium is maintained even under high pressures of hydrogen, and this is in agreement with industrial experience.

The only reference to the effect of cobalt is the work of Houdremont and Schrader,[23] who found that cobalt increases the decarburisation in hydrogen atmospheres.

There seems to be some uncertainty regarding the effect of nickel and copper. Baukloh and Guthman state that copper reduces the depth of decarburisation, while nickel increases it. Bennek, on the other hand, does not agree with these views. It should be indicated, however, that while the former investigator worked with moist hydrogen, the latter used oxidising atmospheres.

The influence which manganese has on the rate of decarburisation is interesting, in that it depends on both the temperature and the carbon content of the steel. Baukloh and Kronenfels have found with

high-carbon steels that at low temperatures there is a gradual increase in the rate of decarburisation with additions of manganese up to 1·2 per cent., but with low-carbon steels the increase in decarburisation reaches a maximum at 0·8 per cent. Mn, higher percentages causing a decrease in the rate of decarburisation. At 1000 deg. Cent. the decarburisation of a steel is not appreciably affected by additions of manganese of the order of 1 or 2 per cent.

Industrial experience has shown that molybdenum increases the decarburisation of a steel and this conclusion is confirmed by a number of investigators[24, 15] working with simple molybdenum steels, and also the more complex high-speed molybdenum steels.

Of the other alloying elements, titanium, zirconium, and at very high temperatures vanadium, decrease the decarburisation of a steel, according to Baukloh and Kronenfels, while tungsten has the opposite effect.

In discussing industrial steels, Schrader points out that the decarburisation found in steels containing small percentages only of the alloying elements, is for all practical purposes the same as with plain carbon steels, both in hydrogen atmospheres and also in the products of combustion of fuels, and it is only with the highly alloyed steels that differences in decarburisation become important.

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The Transformation of Austenite on Quenching

PRODUCTION of high-purity iron at the American National Bureau of Standards has led to several interesting developments. Among them is the study made by T. G. Digges of the critical cooling rates of high-purity iron-carbon alloys. This work was described in the Bureau of Standards *Journal of Research* last year. It revealed, among other points, that the critical rate of cooling required to preserve a martensitic structure in the quenched steel was nearly four times as great in the high-purity steels as in the commercial steels of the same carbon content. The slower critical rate (corresponding to deeper hardening) was mainly due to the higher manganese content of the commercial steels. The work also showed the effect of carbon content. In the iron-carbon alloys of high purity the reciprocal of the critical rate of cooling, *i.e.*, the time to cool from 1100 deg. to 930 deg. Fah., bore a linear relation to the carbon content of the steel. Another factor which affected the critical rate of cooling was grain size, and it was emphasised that constant grain size would have to be secured in specimens intended for the measurement of critical cooling rates if these were to be strictly comparable.

Investigation of the "Transformation of Austenite on Quenching High-Purity Iron-Carbon Alloys" has been continued by Digges[2] in some work which shows the influence of variations of the distribution of carbon in the austenite on the mode and rate of its transformation. The alloys were prepared, as before, by carburising high-purity iron in a mixture of benzene and hydrogen. The iron used contained a total percentage of impurities of 0·030, the elements sulphur, nickel, cobalt, and oxygen accounting for 0·021 per cent. The small specimens of the alloys for test (0·1in. square and 0·040in. thick) were heated electrically *in vacuo*, held at the required temperature for fifteen minutes, and then quenched in a stream of hydrogen.

The initial transformation of a uniform grain of austenite occurs at its grain boundaries which contain the nuclei that are effective in the formation of nodular troostite during the quench. Owing to the presence of these nuclei the austenite in the vicinity of the boundary is least stable and on quenching transforms at a higher temperature than the more stable austenite in the interior of the grains. The smaller grains, after quenching, contained a larger proportion of troostite than the larger grains which had received the same rate of cooling. In other words, the larger the grain size the more stable the austenite and the deeper the hardening of the alloy, a conclusion in agreement with the recognised relationship between austenitic grain size and hardenability. The question of grain size and rate of transformation will form the subject of a later report; the present paper deals mainly with the transformation of non-uniform grains of austenite, which, on account of variations in the distribution and state of solution of the carbon, proceeds at different rates in different regions within the same grain.

By treating a number of samples of the same alloy at the same initial temperature, but cooling to different temperatures before quenching, specimens were secured, having the same average grain size of the parent austenite and the same total carbon content, but varying in the distribution of the dissolved and undissolved carbon at the moment of quenching. A local decrease in carbon content of the austenite causes a decrease in its stability. With low carbon a faster rate of cooling is required to give a completely martensitic structure and, in conformity with this, the temperature of the austenite→martensite change Ar″ was found to be higher. A linear relationship was observed to exist between the temperature of the start of Ar″ and the carbon content, the fall being from 900 deg. to 500 deg. Fah. (482 deg. to 260 deg. Cent.) as the carbon

increased from 0·23 to 0·80 per cent. In hyper-eutectoid austenite, free carbide particles present at the time of quenching, act as nuclei for transformation and increase the reaction rate, or diminish the hardenability, of the austenite. Owing to lack of uniformity the stability of a larger grain is not always greater than that of a smaller. An example is given, in a 1·21 per cent. carbon alloy, of two grains separated at the moment of quenching by a common boundary of cementite. Along this common boundary the smaller grain had transformed to martensite and troostite, the larger to lamellar pearlite. The transformation products of a single large grain of austenite in a 1·14 per cent. carbon alloy included cementite, ferrite, lamellar pearlite, troostite, and martensite. Owing to lack of homogeneity, stability within this grain of austenite did not increase uniformly with distance from the grain boundary as in uniform austenite.

In the course of this investigation use was made of a new form of sensitive diamond indenter for measuring the hardness of micro-constituents. This instrument is described in detail by F. Knoop, C. G. Peters, and W. B. Emerson,[3] and has proved to be extremely useful in distinguishing micro-constituents by their hardness. For example, in passing across the single grain of quenched non-uniform austenite containing 1·14 per cent. of carbon (referred to above) Digges obtained the following values of hardness associated with the microstructures indicated :—

Position.	Micro-hardness number.*	Structure.
1	260	Ferrite and cementite
2	475	Troostite
3	690	Martensite
4	570	Troostite
5	720	Martensite
6	725	Martensite
7	425	Troostite
8	300	Fine pearlite (across lamellæ)
9	190	Coarse pearlite (along lamellæ)

* For the range of hardness shown, the micro-hardness and Brinell numbers agree sufficiently closely to permit consideration of the present values in terms of the more familiar Brinell numbers.

Apart from its use for testing of micro-constituents, this instrument is said to be of value in the testing of very hard and brittle materials, and seems equally well adapted for the testing of electro-deposits and thin sheet metal. Although no extensive study has yet been made of the minimum thickness which may be tested, useful information is said to have been obtained from tests of layers 0·0005in. thick.

An important feature incidentally observed in this work relates to the formation of micro-cracks in martensite. Specimens of the hyper-eutectoid alloys, quenched from high temperatures at rates resulting in complete hardening, often showed numerous fine cracks located not only in the original austenitic grain boundaries, but also in the interior of the grains. Intergranular cracks with respect to the original austenite were also produced in these martensitic specimens by applying sufficient external stress to the quenched material to cause rupture—for example, in making hardness impressions. It appears that even in this very pure material, volume changes associated with the tendency to grain boundary breakdown are responsible for inducing internal stresses which readily lead to micro-cracking. The presence of micro-cracks in high carbon steels may constitute a serious danger as they readily spread under the influence of applied stress, but are difficult to recognise in their original condition, except under the microscope.

REFERENCES

[1] See THE METALLURGIST, August, 1938, 1937–38, 11, 145.
[2] Bureau of Standards, *Journal of Research*, July, 1939, Vol. 23, page 151.
[3] *Ibid.*, page 39.

Books and Publications

Semi-conductors and Metals. By A. H. WILSON. Demy 8vo, pp. viii+120. 1939. Cambridge University Press. 7s. 6d.

MR. A. H. WILSON is well known as a leader in the development of the Theory of Metals. His book bearing that title is a standard work, which only the theoretical specialist can fully appreciate. In the volume now published in the series of Cambridge Physical Tracts, a simplified account is given of some of the main achievements of the theory of metals in the last ten years. This again is not easy reading for anyone but a theoretical specialist. The method of presentation adopted, however, makes a large amount of it readily comprehensible to a reader with good general knowledge and a special interest in the modern electronic theory of metals ; and it can be recommended as an invaluable help to serious students of this subject.

The book is mainly confined to an account of structure in relation to the electrical, thermal, and magnetic properties of metals, and owing to the limitations of space the theory of alloys is only briefly referred to.

What is Steel ? By L. SCHEER. Translated from the third German edition by F. L. MEYENBERG. Demy 8vo, pp. xiv+164. 1939. London : Macdonald and Evans. 6s.

THE provision of books on metallurgy for the non-technical man, or rather for those who do not claim any specialised knowledge of the subject, is a matter of great importance. It has been well done in English by Mr. E. N. Simons and Dr. E. Gregory in their "Structure of Steel Simply Explained." It has also been well done for German readers in "Was ist Stahl ?" by Leopold Scheer. This book, described as "An Introduction for Everyman to the Science of Steel," is deservedly popular in Germany and reached its third edition in a little over a year. The necessity for an English translation is, however, not so clearly evident, and especially for one which so literally follows the form and substance of the German work as to include references to German steels and German standard test pieces exclusively. It is true that kilogrammes per square millimetre have been rendered alternatively as tons per square inch (even when the values refer to Brinell hardness numbers, causing some confusion in the Brinell/tensile ratio), but comparison with British practice and British standards becomes difficult for the non-technical man. Nevertheless, the information is well selected and, on the whole, clearly given. The large Tables I to III form a useful summary of the German standard specifications :—DIN 1661 (Carbon Steels), 1662 (Nickel and Nickel-chromium Steels), and 1663 (Chromium and Chromium-molybdenum Steels).

The book is well produced and contains illustrations of commercial plant and of microstructures as well as numerous constitutional diagrams.